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The Annealing Effect on the Optical and Electrical Properties Nanocrystalline $CuIn_3Se_5$ (OVC)

Neetu Sharma, Rimpy Shukla, Mukesh Jangir, I.P.jain

Centre for Non Conventional Energy Resources,

University of Rajasthan, Jaipur, India 302004

Email: neetu.sha1982@gmail.com

***Abstract*-The ternary chalcopyrite semiconductor $CuInSe_2$ based heterojunction diodes have attracted worldwide interest and emerged as a promising source of energy due to their higher power conversion efficiency. In the present work thin film of Nanocrystalline ordered vacancy compound (OVC) $CuIn_3Se_5$ (OVC) as an absorber layer was used on CdS is reported which is synthesized by chemical bath deposition method at room temperature. The parameters such as temperature, pH and molarity of reactant bath are optimized for achieving homogeneous thin film. As-deposited film is annealed at different temperature in the range 150-250^oC in air for one hour and then characterized by UV –Vis measurements and IV measurements for finding the optical, electrical properties respectively. The nanostructure morphology of OVC and $CuInSe_2$ is observed onto the Nanocrystalline phase of CdS.**

***Keywords*- Nanocrystalline, $CuIn_3Se_5$, ordered vacancy compound, Thin film, ion exchange reaction, optical properties, electrical properties.**

I. INTRODUCTION

Ternary chalcopyrite compound $CuIn_3Se_5$ is a promising material for photovoltaic application which belongs to the family of ordered vacancy compounds (OVC) having properties nearly similar to ternary compound $CuInSe_2$. It has attracted much attention due to interesting properties with the direct optical band gap value of about 1.3 eV [1] close to the optimal value of 1.4 eV, high photoconductivity over a broad wavelength range [2], large absorption coefficient ($10^4 cm^{-1}$) and direct inter-band transitions which makes it a leading material for high efficiency solar energy conversion [3]. Both bulk and thin film material find wide practical application [4-9] .The structure of $CuIn_3Se_5$ can be derived from that of the chalcopyrite $CuInSe_2$ with an ordered array of copper vacancy or defect pair so the compound is called order defect compound or ordered vacancy compound [10]. The OVC occurs within the interface surface layer of the $CuInSe_2$ in high efficiency polycrystalline solar cell and on the other hand this compound is less studied in comparison with $CuInSe_2$ in the pseudo –binary system Cu_2Se-In_2Se_3.

Hence the main purpose of the reported work is to study the different properties of $CuIn_3Se_5$ by annealing it at different temperature range. There are several methods viz chemical and physical for the synthesis of the varying composition of $Cuinse_2$ to form orderd vacancy compound [11-13]. In the present work Nanocrystalline $CuIn_3Se_5$ thin film were prepared using alkaline chemical solution growth technique at room temperature on to a glass and ITO substrate having pre deposited CdS thin film which has been used as a window material due to its high band gap energy (2.54eV) which enhances the performance by omitting the absorbance loss [14,15]. The cation and anion exchange reaction of Cd^{+2} and S^{2-} is occurred with Cu^{+2}, In^{3+}, Se^{2-} ions respectively in alkaline chemical bath. The uniformity and desired nanostructure can be achieved by optimize the synthesis parameter such as pH, reaction bath temperature, time and concentration of the reactants.

II. EXPERIMENTAL PROCEDURE

Synthesis of nanostructure thin film of $CuIn_3Se_5$ (ordered vacancy compound) takes place in two step. In

the first step dark yellow CdS thin film is deposited on to both glass and ITO substrate at 80^0 C for 1 hour by simple wet chemical bath deposition method using cadmium chloride ($CdCl_2$).(01M) and thiourea NH_2CSNH_2(.01M) as reactants while pH of the mixture was kept ≈11 by the addition of ammonia solution. Then the CdS thin film was annealed at 200^0C for one hour. In the second step the pre-deposited annealed thin film of CdS is used for deposition of $CuIn_3Se_5$ in alkaline bath by using $CuCl_2$ (.02M), ammonia solution, thiourea (.03M), $InCl_3$ (.02M), and sodiumselenosulphite Na_2SeSo_3 (0.03M). Na_2SeSo_3 solution was obtained by refluxing elemental selenium and sodium sulphate in water. The three drops of triethenolamine (TEA) is used in $CuCl_2$and $InCl_3$ solution for controlling the metallic ion exchange reaction at relatively lower rates and for avoiding the metal oxide formation within the solution. All the three solution were mixed and stirrer about five minutes for getting a clear homogeneous solution while pH value of the solution was kept ≈11. After one hour the yellow film of the CdS is converted into the dark blackish film. Then the as-deposited film is annealed in air in the range 150^0 C to 250^0 C for one hour.

III. CHARACTERIZATION TECHNIQUES

Thin films of the $CuIn_3Se_5$ are characterized for optical and electrical properties. The thickness of the film is measured by gravimetric method. To study the optical characteristics of the film absorbance spectra was recorded in the range 300-1100nm by U 2900 Hitachi UV-Vis spectrometer. The IV measurements were studied using our laboratory equipment unit over the range from ±1eV.

A. Optical Analysis

Fig.(1) and Fig (2) (a), (b), (c) show the UV-Vis absorption spectra of as-deposited ,150^0C and 250^0C annealed film respectively. The energy band gap of the film can be found by help of the following equation for the direct allowed transition

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

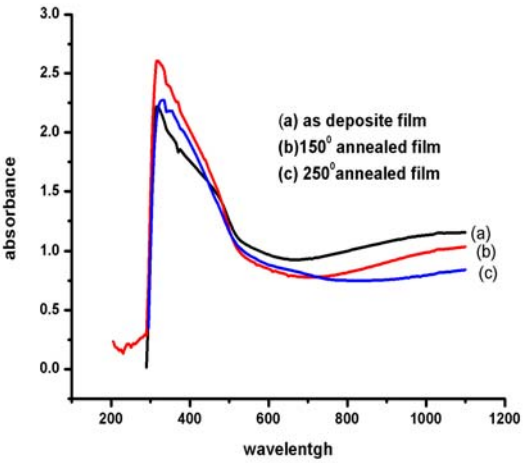

Fig.1

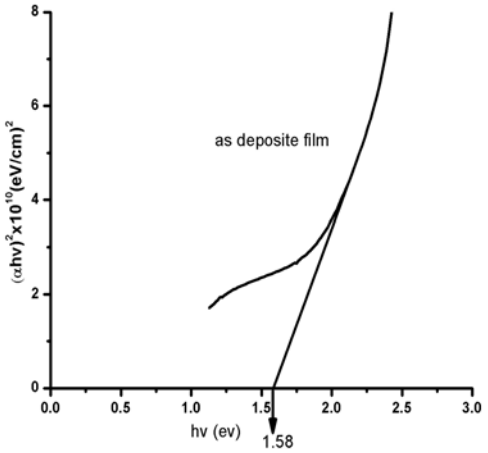

Fig.2 (a)

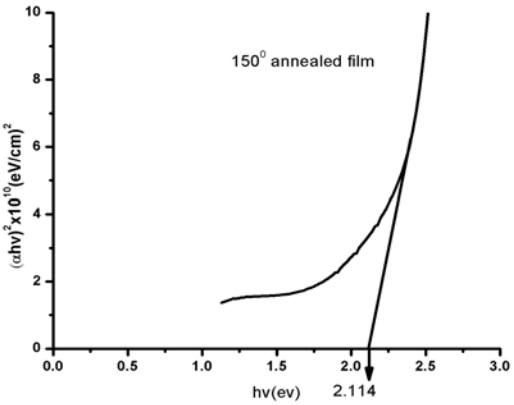

Fig.2 (b)

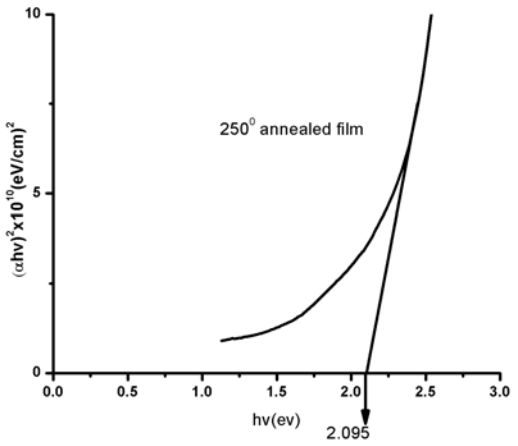

Fig.2 (c)

Where A is the constant and E_g is the band gap, $h\nu$ is the photon energy.

Graph between $(\alpha h\nu)^2$ and $h\nu$ having the straight line with the photon energy axis intercept giving the value of the band gap. The variation of $(\alpha h\nu)^2$ and $h\nu$ having straight line indicating direct transition of the carriers. The band gap Eg is determined by the extrapolating the straight line portion to the energy axis. So the band gap is varying with the annealing of the $CuIn_3Se_5$ at different temperature. The reported value of the direct band gap of OVC lies between 1.20-1.31eV so the increment of the direct band gap occurs due the finally resultant phase of OVC (CdS) by the ionic exchange reaction between $CuInSe_2$ and CdS [17]and nano crysatlline nature of the film .

B. Electrical Analysis

Fig 3 shows the IV characteristic curve for the different films deposited at room temperature for dark current.

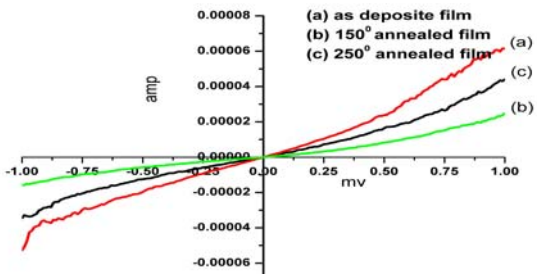

Fig.3 IV measurements of $CuIn_3Se_5$ used for electrical analysis (a)as-deposit film (b)150^0 C (c)250^0C annealed film

The nature of the graph is semiconductor in behavior and the resistance of the $CuIn_3Se_5$ varying with the annealing of the film.

IV. CONCLUSION

This film of the $CuIn_3Se_5$ has been deposited successfully by chemical bath deposition method. Optical band gap varies with annealing of the film. The dark current also changes with the annealing of the film Therefore this film are useful for thin film solar cell as an absorber layer.

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